NOTIZEN

Effect of Various Cations and Anions on the Reduction of Molybdenum (VI) at D.M.E. and its Determination in their Presence

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(Z. Naturforsch. **24 b**, 1053—1055 [1969]; eingegangen am 21. April 1969)

In earlier publication¹, the authors have reported data on the polarographic behaviour of molybdenum(VI) in three different organic acid media viz. mandelic acid, succinic acid and formic acid — sodium formate and concluded that in medium comprised of 0.1 M mandelic acid, 0.005% thymol and 0.1% camphor Mo(VI) produces a well defined irreversible diffusion controlled doublet wave, the total height of which varies linearly with Mo(VI) concentration. In view of the difficulties associated with the polarographic determination of Mo(VI) because of the lack of appropriate supporting electrolytes in which the waves are well formed with diffusion current proportional to concentration and due to the occurrence of analytically useful wave in mandelic acid medium it was considered worthwhile to investigate the effect of the presence of various cations and anions on the Mo(VI) wave and the possibility of its determination in their presence.

The present communication, therefore, describes data on the effect of the presence of Ni^{2+} , Co^{2+} , WO_4^{2-} , VO_3^- , $\text{Cr}_2\text{O}_7^{2-}$, Mn^{2+} , TeO_4^{2-} , Fe^{3+} , Ti^{2+} , ClO_4^- , NO_3^- , on the wave produced by molybdenum(VI).

Experimental

Anal.R. (BDH) reagents, sodium molybdate, mandelic acid, thymol, camphor and soluble compounds of cations and anions under study were used and their solutions prepared in air-free conductivity water.

A manual polarograph with Scalamp galvanometer as a current recorder was used in these investigations. A capillary having the following characteristics $m = 3.58 \text{ mg/sec}$, $t = 2.416 \text{ sec}$, $m^{2/3} t^{1/6} = 2.226 \text{ mg}^{2/3} \text{ sec}^{-1/6}$, was used in conjunction with saturated calomel electrode connected to the cell by low resistance salt bridge. The potentials applied with the aid of polarograph were further checked against a vernier potentiometer and were found to differ not more than 3—4 mV from the indicated values. Unless otherwise stated, all measurements were

done with the H-cell immersed into a thermostatic bath controlled at $28^\circ \pm 0.1^\circ \text{C}$. Purified hydrogen was bubbled through the solution for fifteen minutes before the start of each recording, and was passed over the solution during the measurements.

Results and Discussion

In these investigations the attention has been focussed mainly on the effect of various cations and anions upon diffusion controlled irreversible doublet wave produced by Mo(VI) in 0.1 M mandelic acid medium and on the possibility of developing a rapid and accurate method for the determination of Mo(VI) in solution. For the removal of interfering steps camphor has been used as an electrochemical masking agent².

Effect of tungsten(VI) and chromium(VI). The polarography of Mo(VI) has been studied mainly in presence of mineral acids³⁻⁶ and its determination in presence of its group elements Cr(VI) and W(VI) has been rarely reported owing to the almost similar behaviour of Cr(VI) and W(VI)⁷⁻⁹. Mandelic acid, comparatively, has been found to be more fruitful; in this medium tungsten(VI) does not produce any wave and the height of Mo(VI) wave changes linearly with its concentration. Fig. 1 curve I illustrates the i_d -concentration plot, which clearly indicates the strict linearity.

Fig. 1. Plots of " i_d " vs. concentration of Mo(VI) in presence of W(VI), Cr(VI) and Fe(III).

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<i>In presence of Chromium(VI)</i>					
Mo(VI) present [mg]	95.95	38.38	19.19	9.595	4.797
W(VI) present	367.70	367.70	183.85	183.85	91.92
Mo(VI) found	97.73	37.86	19.32	9.633	4.909
Error	1.750	0.520	0.130	0.038	0.112
<i>In presence of Tungsten(VI)</i>					
Mo(VI) present	191.91	95.95	47.97	19.19	
Cr(VI) present	52.00	52.00	26.00	52.00	
Mo(VI) found	197.45	98.71	49.05	20.11	
Error	5.54	2.76	1.08	0.92	
<i>In presence of Iron(III)</i>					
Mo(VI) present	95.95	47.97	19.19	47.97	
Fe(III)	55.85	55.85	55.85	223.40	
Mo(VI) found	91.52	45.64	17.85	45.89	
Error	4.43	2.33	1.34	2.08	

Table 1. Polarographic determination of Mo(VI).

A series of mixtures containing different concentrations of Mo(VI) (1–0.05 mM) and W(VI) (2–0.5 mM), 0.1 M mandelic acid, 0.005% thymol and 0.1% camphor were synthesised; the mixtures were then polarographed as such and after adding a known volume of standard solution (5 mM Na_2MoO_4). The corresponding “ i_d ” values were determined after allowing necessary correction for residual current, which was obtained by drawing a polarogram of a blank solution. The reliability of the method is shown by the data in Table I.

It is evident from Table I that Mo(VI) in presence of tungsten can be determined down to 0.05 mM with an accuracy of 2 per cent.

Chromium(VI) at zero applied potential produces appreciable diffusion current in mandelic acid medium in absence of camphor and no wave was observed up to -1.2 V (vs. S.C.E.) but camphor (0.1%) reduces the magnitude of “ i_d ” to its one fourth value and makes current variations more regular (Fig. 2). A solution containing Mo(VI) and Cr(VI) in presence of camphor was polarographed, which yielded a well defined two step

Fig. 2. C-V curves of 1 mM $\text{K}_2\text{Cr}_2\text{O}_7$ in 0.1 M mandelic acid + 0.005% thymol; (I) in absence of camphor, (II) in presence of 0.1% camphor and (III) in presence of 0.1% camphor + 2 mM Na_2MoO_4 .

polarogram due to the reduction of Mo(VI) (Fig. 2, curve III). The electrochemical masking agent (camphor) thus makes it possible to determine the Mo(VI) in presence of chromium. A series of polarograms of solutions containing varying amounts of Mo(VI) (2–0.2 mM) and Cr(VI) (1–0.5 mM) were recorded; the proportionality between “ i_d ” and “C” was checked (Fig. 1, curve II). The various mixtures were prepared and analysed by using standard addition method¹⁰. The results obtained have been summarised in Table I.

Effect of Vanadium(V) and Iron(III). Fig. 3, curves I and II, represents C–V curves of 1 mM NaVO_3 in 0.1 M mandelic acid and 0.005% thymol in presence and absence

Fig. 3. C-V curves of 1 mM NaVO_3 in 0.1 M mandelic acid + 0.005% thymol; (I) in absence of camphor, (II) in presence of 0.1% camphor, and (IV) in presence of 2 mM Na_2MoO_4 + 0.1% camphor. Curve III. Polarogram of 2 mM Na_2MoO_4 in 0.1 M mandelic acid + 0.005% thymol + 0.1% camphor.

¹⁰ L. MEITES, “Polarographic Techniques” Interscience Publishers, Inc., New York 1955, p. 178.

S.No.	Mo(VI) present [mg]	Concen. of other cations and anions	Mo(VI) found [mg]	Error [mg]
1	95.95	2 mM $\text{Cr}_2\text{O}_7^{2-}$, 1 mM Fe^{3+} , 2 mM Mn^{2+} , 2 mM Ni^{2+} , 2 mM WO_4^{2-} , 2 mM Co^{2+} , 2 mM TeO_4^{2-}	103.73	7.78
2	38.38	2 mM $\text{Cr}_2\text{O}_7^{2-}$, 1 mM Fe^{3+} , 2 mM Mn^{2+} , 2 mM Ni^{2+} , 2 mM WO_4^{2-} , 1 mM Co^{2+} , 2 mM TeO_4^{2-}	42.45	4.07
3	27.41	0.5 mM $\text{Cr}_2\text{O}_7^{2-}$, 0.5 mM Fe^{3+} , 1 mM Mn^{2+} , 1 mM Ni^{2+} , 1 mM WO_4^{2-} , 1 mM Co^{2+} , 1 mM TeO_4^{2-}	29.58	2.17

Table II. Determination of Mo(VI) in presence of various cations and anions.

of camphor and curves III and IV are the polarograms of 2 mM Mo(VI) and 2 mM Mo(VI) + 1 mM V(V) in the same medium containing 0.1% camphor. It is evident from the curve I that the diffusion current starts from the zero applied potential itself; obviously, owing to the greater value of potential of the $\text{V}^{5+}-\text{V}^{4+}$ couple (+ 0.7 V. VsSCE) than the oxidation potential of the mercury; then after exhibiting slight rounded maximum in the potential range - 0.3 to - 0.4 V a ill defined wave starts from about - 0.6 V. In presence of camphor, however, the magnitude of the diffusion current decreases and ill defined wave shifts to more negative potentials. A comparison of the curves III and VI makes it clear that in presence of V(V) enhancement of the first step of Mo(VI) doublet wave takes place, which may probably be due to some catalytic phenomenon. Almost similar type of observation was also experienced by KENNEDY and JENSEN¹¹ while studying the effect of Mo(VI) on the reduction of V(V) in E.D.T.A. Owing to the catalytic effect the height of Mo(VI) wave does not show linear relationship with concentration and hence a medium comprised of 0.1 M mandelic acid, 0.005% thymol and 0.1% camphor does not permit the determination of Mo(VI) in presence of V(V). The detailed investigations on this system are, however, in progress.

Iron(III) has been found to be inert at d.m.e. in mandelic acid medium in presence of camphor. In its presence the height of Mo(VI) wave varies linearly with concentration (Fig. 1, curve III). The table I cited above illustrates the results of analysis of different synthetic mixtures and reliability of the method.

Effect of Ni(II), Co(II), Mn(II), TeO_4^{2-} , Ti(II) , UO_2^{2+} , ClO_4^- and NO_3^- . The cations Ti^{2+} and UO_2^{2+} have been found to produce waves in mandelic acid medium

in potential range covered by Mo(VI) wave even in presence of higher concentrations of camphor and consequently interfere seriously. In 0.1 M mandelic acid, therefore, Mo(VI) cannot be determined in presence of Ti^{2+} and UO_2^{2+} . The cations and anions viz. Ni^{2+} , Co^{2+} , Mn^{2+} , TeO_4^{2-} and NO_3^- have been found to be absolutely inert at d.m.e. and Mo(VI) in their presence can be estimated polarographically. It is noteworthy that NO_3^- and ClO_4^- produce serious catalytic effects in acidic medium^{12,13} but are inactive in medium employed for present investigation.

A possibility of estimating Mo(VI) in presence of various cations and anions viz. WO_4^{2-} , CrO_7^{2-} , Fe^{3+} , Ni^{2+} , Co^{2+} , Mn^{2+} , TeO_4^{2-} has been studied. A series of mixtures containing appropriate concentrations [2–4 times more than Mo(VI) concentration] of above mentioned ions and different concentrations of Mo(VI) were synthesised and polarographed. Standard addition method was employed for determining Mo(VI) contents in synthetic mixtures. All diffusion current data were secured at a fixed potential i.e. - 0.9 volts (vs. S.C.E.). Table II given below illustrates the results obtained and the accuracy of the method.

Observations recorded above (Table II) indicate clearly that the Mo(VI) in presence of various cations and anions can be determined successfully. The determination of Mo(VI) contents below 25 mg/l has not been found possible. Higher concentrations of Fe(III) and Cr(VI) interfere and should be avoided.

I wish to express my gratitude to my teacher, Prof. Dr. R. S. SAXENA, D. Sc., Ph. D., F.R.I.C. (London), who interested me in polarography, put the best working facilities at my disposal, and stimulated this work by many valuable suggestions.

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